Supporting Information

Thermochromism of Model Organic Aerosol Matter

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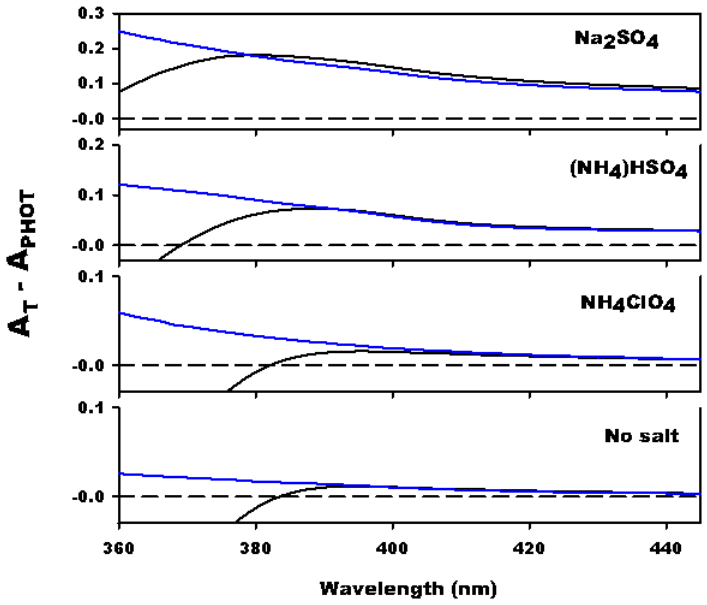

FIGURE S1. Absorbances of the photolyzed solution after 19h at 25°C in the dark (A_T) minus absorbances before photolysis (black solid line), or after photolysis for 2h (blue line) (A_{PHOT}) of 70mM PA solutions in the absence, and presence of 1.5M Na_2SO_4, 2M NH_4HSO_4 (ABS), or 2M NH_4ClO_4

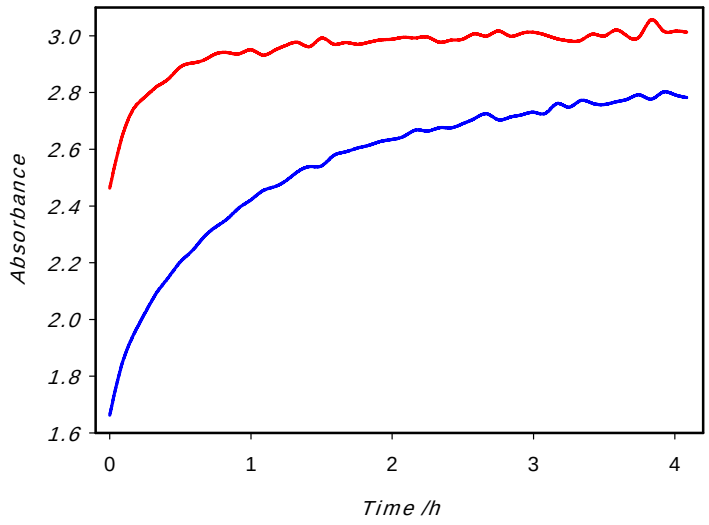

FIGURE S2A. Absorbances A_λ vs. time in a 120 mM PA solution previously photolyzed for 4.5 h, after diluting it by half with 4 M ABS, and then heated at 60°C. λ = 290nm (red trace); 300nm (blue trace). Curves closely follow exponential growth kinetics: $A_\lambda(t) = A_\lambda(\infty)\,[1 - \exp(-k_\lambda\, t)]$; See text.

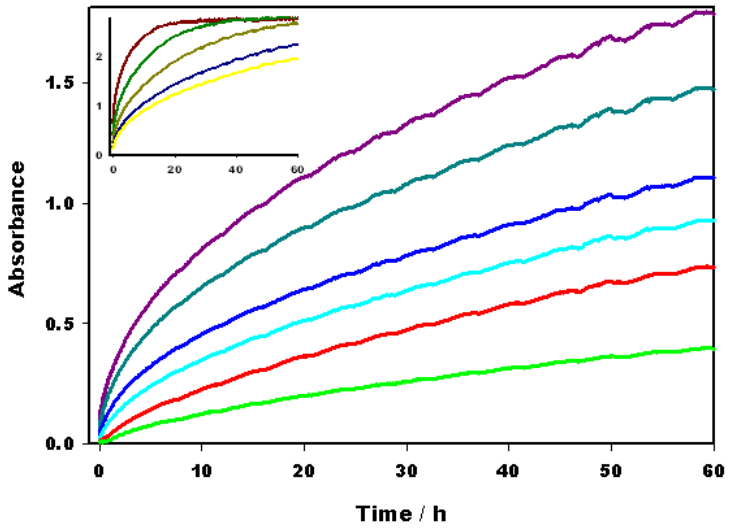

FIGURE S2B. Absorbances A_λ vs. time in a 60 mM PA, 2M ABS solution previously photolyzed for 4.5 h, maintained in the dark at 60°C. From the top: λ = 350, 360, 380, 400, 450 and 500 nm. Inset, from the top: λ = 310, 320, 330, 340 and 346 nm. See text.

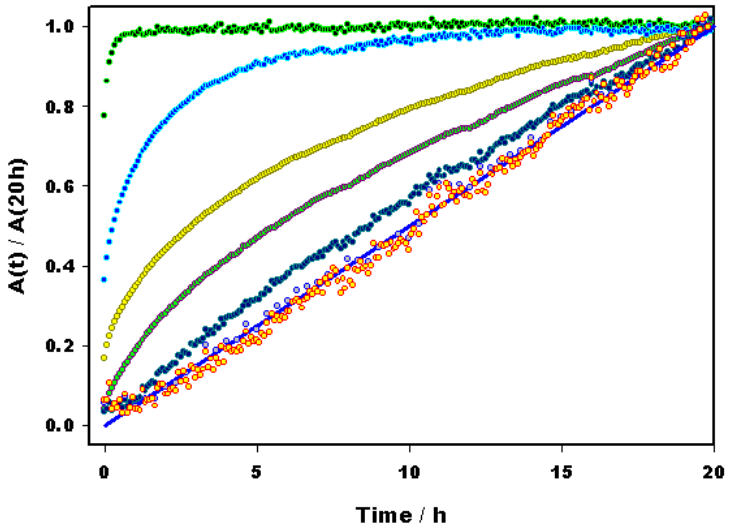

FIGURE S3. Normalized absorbances $A_\lambda(t)/A_\lambda(20h)$ vs. time of a previously photolyzed (for 4.5 h) 60 mM PA, 2M ABS solution, maintained in the dark at 60 °C. From the top: λ = 280, 320, 300, 400, 420, 450, 560 and 650 nm.

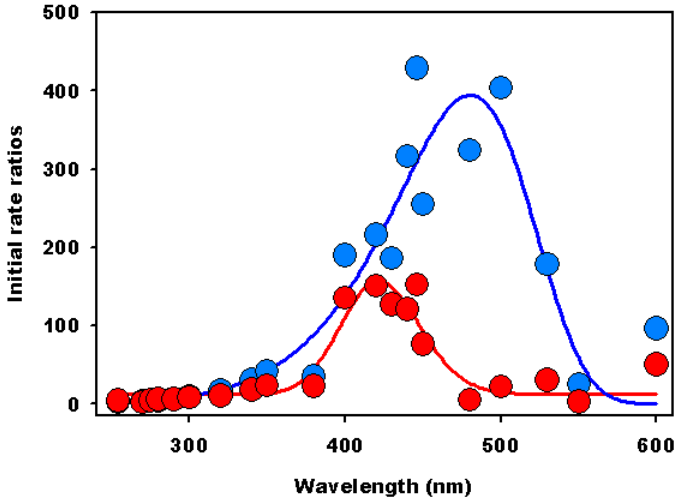

FIGURE S4. Ratios of initial rates ${}^{ABS}[\partial A_\lambda(t)/\partial t]_0/[\partial A_\lambda(t)/\partial t]_0$ in experiments involving 62 mM PA solutions previously photolyzed for 4.5 h, in the absence $\{[\partial A_\lambda(t)/\partial t]_0\}$ or presence $\{{}^{ABS}[\partial A_\lambda(t)/\partial t]_0\}$ of 2M ABS. Red circles and line: in stage (C). Blue circles and line: after the second thermal treatment, stage (D). See main text.

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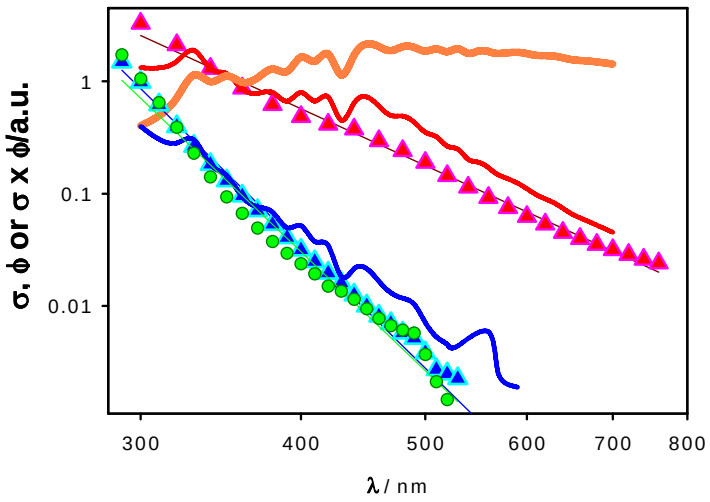


FIGURE S5. Solar energy fluxes $\phi(\lambda)$ at the Earth's surface at zero zenith angle (bold orange curve). Absorption cross sections $\sigma(\lambda)$ and $\sigma(\lambda)\times\phi(\lambda)$ products for a 60 mM PA, 2M ABS solution, after stage (D) (re-photolysis) [$\sigma_D(\lambda)$, blue triangles], [$\sigma_D(\lambda)\times\phi(\lambda)$, bold blue curve], followed by thermal treatment for 21h at 60 °C [$\sigma_C(\lambda)$, red triangles], [$\sigma_C(\lambda)\times\phi(\lambda)$, bold red curve]. 60mM PA, 2M ABS solution after stage (C) at 25C for 12h; [$\sigma(\lambda)$, green circles].

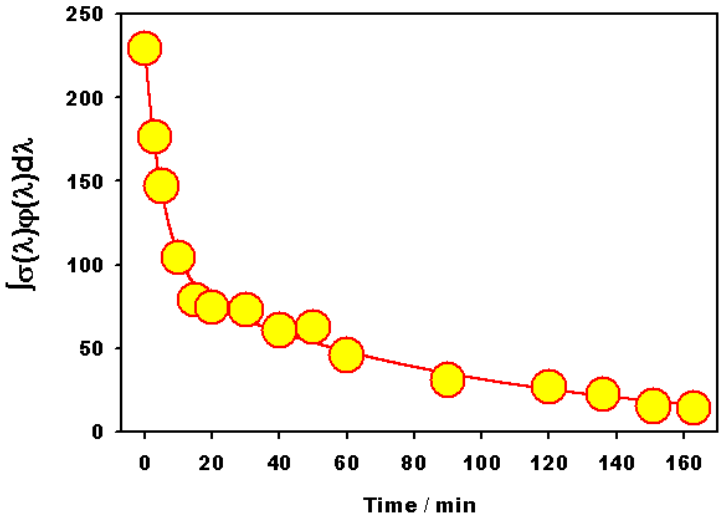
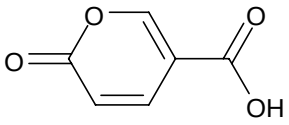


FIGURE S6. $\int_{300}^{700}\sigma(\lambda)\phi(\lambda)d\lambda$ during the photobleaching of a 80m MPA, 2M ABS solution after stage (C). See text.

Chemicals and Procedures

Ammonium bisulfate (ABS, Fluka >99%), sodium sulfate (EMD Chemicals, 99%), ammonium perchlorate (Mallinckrodt, 99%) salts were used as received. 1 M sulfuric acid (VWR) was used to adjust the pH of the solutions as indicated. All solutions were made in deionized, ultrapure water (resistivity 18.2 MΩ cm) from a Millipore purification system. Salts were added to PA solutions prior to, or immediately after photolysis, as indicated.

Negative ion mass spectra of directly infused sample solutions (previously diluted with chromatographic grade methanol, Chromasolv, purity > 99.9%) were acquired using a ± 0.1 Da resolution electrospray ionization mass spectrometer (Agilent 1100). Sample solutions were also analyzed via HPLC-MS in a system provided with tandem UV-detection a (Hewlett-Packard 1100 series) using a Nova-Pak C18 column (300 m × 3.9 mm, Waters). The eluents were 92.5% of 0.1% acetic acid in water solution (A) and 7.5% methanol (B). B programmed to increase linearly from 7.5% to 90.0% between 8 and 45min.



coumalic acid

Scheme S1